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Coffie, S., Hogg, J. M., Cailler, L., Ferrer-Ugalde, A., Murphy, R. W., Holbrey, J. D., Coleman, F., & Swadzba-Kwasny, M. (2015). Lewis Superacidic Ionic Liquids with Tricoordinate Borenium Cations. *Angewandte Chemie International Edition*, 54(49), 14970-14973. <https://doi.org/10.1002/anie.201508653>

Published in:
Angewandte Chemie International Edition

Document Version:
Early version, also known as pre-print

Queen's University Belfast - Research Portal:
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This is the pre-peer reviewed version of the following article: Coffie, S., Hogg, J. M., Cailler, L., Ferrer-Ugalde, A., Murphy, R. W., Holbrey, J. D., Coleman, F. and Swadzba-Kwasny, M. (2015), Lewis Superacidic Ionic Liquids with Tricoordinate Borenium Cations. *Angew. Chem. Int. Ed.*, 54: 14970–14973. doi:10.1002/anie.201508653, which has been published in final form at <http://onlinelibrary.wiley.com/doi/10.1002/anie.201508653/abstract>.

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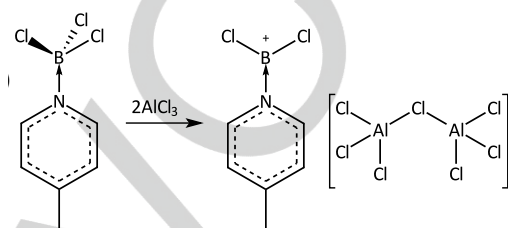
Lewis superacidic ionic liquids with tricoordinate borenium cations

Sesime Coffie, James M. Hogg, Lucie Cailler, Albert Ferrer-Ugalde, Richard W. Murphy, John D. Holbrey, Fergal Coleman,* and Małgorzata Swadźba-Kwaśny*

Abstract: The first examples of ionic liquids based on borenium cations, $[\text{BCl}_2\text{L}]^+$, are reported. These compounds form solvent-free highly Lewis acidic liquids. Acidity was quantified using the Gutmann Acceptor Number (AN) method with extremely high ANs recorded (up to AN = 182, $\delta_{31\text{P}} = 120$ ppm) demonstrating that these borenium ionic liquids are the strongest Lewis superacids reported to date.

Borocations are important reagents in organic synthesis (*viz.* C–H borylations^[1] or alkene hydroboration^[2]) and as Lewis acidic components in frustrated Lewis pairs.^[3] Their chemistry has been reviewed by Kölle and Nöth,^[4] and more recently by Piers *et al.*^[5] and Ingleson.^[6] Chemistry of tricoordinate borenium cations, which are the focus of this work, have been reviewed by De Vries *et al.*^[7] Borenium ions are very strong Lewis acids, with the electron deficiency of the vacant boron *p* orbital enhanced by the positive charge. The most important routes to generate borenium cations are hydride or halide abstraction from tetracoordinate boron adducts, $[\text{BX}_3\text{L}]$, using an excess of abstracting agent (Figure 1).^[4,5,7,10]

Many borenium complexes have been reported as ‘oily materials’.^[4] Despite the increasing number of known crystal structures,^[5,8,9] they are generally difficult to crystallize, and are typically studied in solution, using ^{11}B NMR spectroscopy. We hypothesised that these ‘oily materials’ might be in fact ionic liquids. Studying them in this form may enable access to ‘naked’ borenium cations in which the full Lewis acidity of the boron centre could be harnessed without detrimental solvent effects. Ionic liquids are salts with low lattice energies and low melting points (arbitrarily below 100 °C) and can be generated by selecting ions with low symmetry, and with low charge which is preferably dispersed across multiple sites.^[11] The borenium salt shown in Scheme 1 contains a large anion of low symmetry and a charge-dispersed cation, exemplars for ionic liquid formation. Continuing our effort to develop strongly Lewis acidic systems from off-the-shelf reactants,^[12–14] liquid borenium salts have been prepared, their speciation determined and Lewis acidity measured.



Scheme 1. The formation and structure of a borenium cation with $[\text{Al}_2\text{Cl}_7]^-$ anion

Boron adducts. $[\text{BCl}_3\text{L}]$, with L-type ligands of differing donor characteristics were isolated as colourless powders. Aromatic *N*-donors (pyridine, py; 3-picoline, 3pic; 4-picoline, 4pic; and 1-methylimidazole, mim) were selected as particularly suitable for the stabilisation of borenium cations, due to their σ -donor properties.^[15] For structural comparison, an adduct with an aliphatic base (trioctylphosphine, P_{888}) was prepared; the phosphine is a stronger donor to BCl_3 than the corresponding amine.^[16] ^{11}B NMR spectra (Figure 1-SI, Table 1-SI) were in agreement with the literature.^[16,17]

Borenium ionic liquids were prepared *via* a solventless procedure, analogous to that used for chlorometallate ionic liquids.^[18] All products were homogenous liquids, except for equimolar mixtures of $[\text{BCl}_3(\text{mim})]$ and MCl_3 , which formed white pastes. Aluminium(III) chloride was used in 1 or 2 mol ratio with respect to $[\text{BCl}_3\text{L}]$ adducts, because only two chloroaluminate(III) anions exist in homogeneous ionic liquids: $[\text{AlCl}_4]^-$ and $[\text{Al}_2\text{Cl}_7]^-$.^[19,20] In contrast, higher chlorogallate(III) anion homologues are known,^[20,21] so gallium(III) chloride was used in 1–3 mol ratio.

A major peak in the ^{11}B NMR spectra was observed at 30–50 ppm (Table 1-SI). The shift depended on $[\text{BCl}_3\text{L}]$ to MCl_3 stoichiometry, but not on the metal (Al or Ga), with the signals shifted upfield for systems with 1:1 stoichiometry compared to those with 1:2 (Figure 2-SI). This revealed incomplete halide abstraction using 1 mol eq. of MCl_3 , and complete ionisation with 2 or 3 mol eq. of MCl_3 , in agreement with solution studies.^[9,10] For L- BCl_3 -2 MCl_3 systems, the main feature was a broad peak at 44 ± 4 ppm, corresponding to formation of tricoordinate $[\text{BCl}_2\text{L}]^+$ cations.^[5,7] A shoulder at 45 ± 1 ppm indicates the presence of BCl_3 , and consequently partial exchange of the ligand to Al or Ga centres.^[9,22] Similarly, the main signal at 36 ± 1 ppm and shoulder *ca.* 45.5 ppm for P_{888} - BCl_3 -2 MCl_3 systems is consistent with $[\text{BCl}_2\{\text{P}_{888}\}]^+[\text{MCl}_4]^-$ and BCl_3 .

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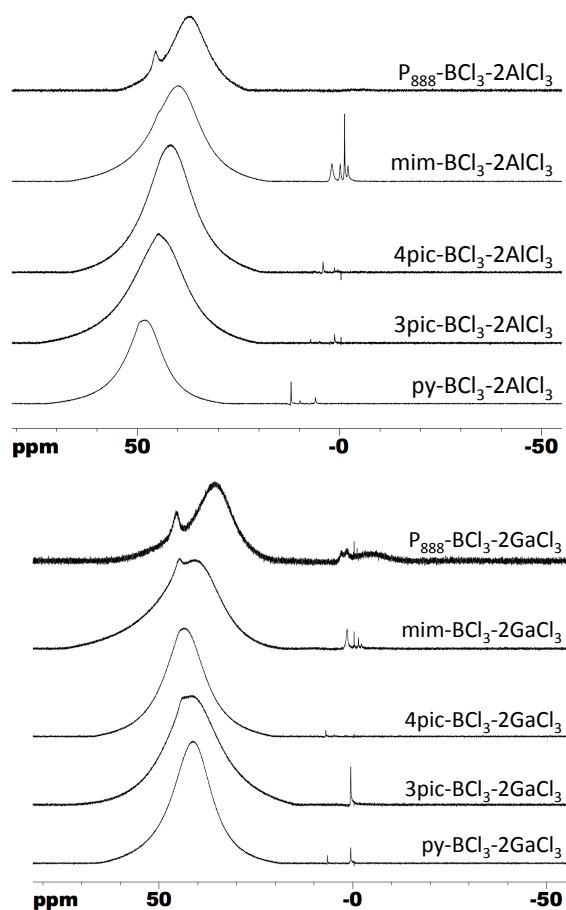


Figure 1. ^{11}B NMR spectra (128.37 MHz, 27 °C, neat liquid with $\text{DMSO-}d_6$ lock) of borenium ionic liquids of a general formula $\text{L-BCl}_3\text{-2MCl}_3$, where $\text{M} = \text{Al}$ (top) and Ga (bottom)

Partial ligand transfer onto a metal centre was confirmed with ^{27}Al NMR spectroscopy (Figure 3-SI, Table 2-SI). For *N*-donors, the main signal at ca. 106 ppm was found, corresponding to equilibrated tetracoordinate complexes: $[\text{AlCl}_4]^-$, $[\text{Al}_2\text{Cl}_7]^-$, and $[\text{AlCl}_3\text{L}]^{[24-26]}$ with a shoulder at 75 ± 1 ppm, originating from a pentacoordinate complex, $[\text{AlCl}_3\text{L}_2]$, and/or cationic complex, $[\text{AlCl}_2\text{L}_2]^+$. $^{[25,27]}$ ^{27}Al NMR spectrum of $\text{P}_{888}\text{-BCl}_3\text{-2AlCl}_3$ gave a broad feature with two maxima at 66 and 114 ppm, consistent with species analogous to those identified for *N*-donors. $^{[12],[28]}$

The crystal structure of $[\text{BCl}_2(\text{py})][\text{AlCl}_4]$, isolated here as an ionic liquid, has been reported. $^{[9]}$ This indicates that some systems described in this work may be in fact supercooled liquids. $^{[29]}$ It is also likely that dynamic equilibria with other than $[\text{BCl}_2\text{L}]^+$ and $[\text{MCl}_4]^-$ components (metal complexes, BCl_3) hinder the crystallisation.

Lewis acidity of borenium ionic liquids was quantified by the Gutmann Acceptor Number (AN), where triethylphosphine oxide (tepo) is used as a ^{31}P NMR probe. In AN scale, hexane has $\text{AN} = 0$, SbCl_5 in 1,2-dichloroethane has $\text{AN} = 100$, and acids with $\text{AN} > 100$ are considered Lewis superacids. The

method is well established in Lewis acidity studies of both borenium cations $^{[7,22]}$ and of ionic liquids. $^{[18,20]}$ Unambiguous results could only be obtained for systems with *N*-donors, because the ^{31}P NMR signals from tepo (used in 1–3% quantity) were obscured by signals from the P_{888} ligand.

AN values were calculated based on the signal originating from $[\text{BCl}_2\text{L}(\text{tepo})]^+$ (Table 2). ^{31}P NMR chemical shifts measured for 1% tepo solutions, $\delta_{31\text{P}}^{1\% \text{ tepo}}$, were also reported. All the AN values fall within the Lewis superacidity region, $\text{AN} = 120\text{--}182$. Al-containing systems gave two primary ^{31}P signals (Figure 2, bottom). The more upfield signals ($\delta_{31\text{P}}^{1\% \text{ tepo}} = 84 \pm 2$ ppm; $\text{AN} = 96 \pm 2$) were consistent with tepo coordinating to the Al centre. $^{[18,30]}$ The downfield signals ($\delta_{31\text{P}}^{1\% \text{ tepo}} = 94.5\text{--}117.2$ ppm; $\text{AN} = 120\text{--}174$) correspond to tepo coordinating to the borenium cation. In $\text{L-BCl}_3\text{-}n\text{GaCl}_3$ systems ($n = 1$ or 2) only one main signal was detected, consistent with tepo coordinated to a borenium cation (Figure 2, top). With three moles of GaCl_3 , a second signal appeared ($\delta_{31\text{P}}^{1\% \text{ tepo}} = 93 \pm 1$ ppm; $\text{AN} = 118 \pm 1$), at a slightly higher value than that reported for chlorogallate(III) ionic liquids with $[\text{Ga}_3\text{Cl}_{10}]^-$ anion ($\text{AN} = 107$). $^{[18]}$

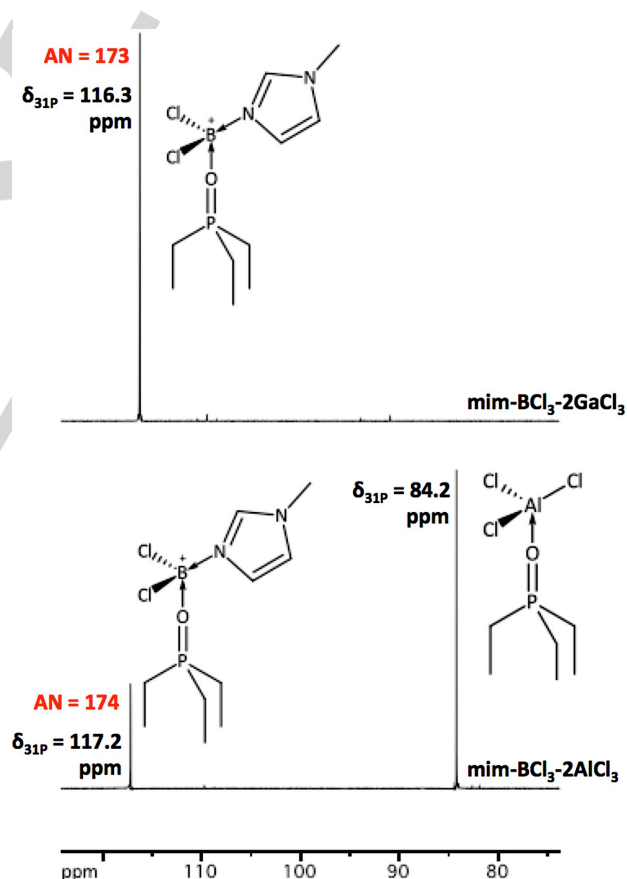


Figure 2. ^{31}P NMR spectra (161.96 MHz, 27 °C, neat liquid with $\text{DMSO-}d_6$ lock) of 1% tepo solution in borenium ionic liquids of a general formula $\text{mim-BCl}_3\text{-2MCl}_3$

Table 1. AN values for all L-BCl₃-nMCl₃ systems based on N-donors, which were homogenous liquids, along with δ_{31P} signals measured for 1% solution of tepo in these liquids (referred to δ_{31P} H₃PO₄ 85% = 0.0 ppm).

L (pK _a)	AlCl ₃		2AlCl ₃		GaCl ₃		2GaCl ₃		3GaCl ₃	
	AN	δ_{31P}	AN	δ_{31P}	AN	δ_{31P}	AN	δ_{31P}	AN	δ_{31P}
py (5.12)	120	94.5	162	109.6	121	94.7	134	99.9	180	119.2
3pic (5.63)	124	95.5	170	113.2	121	95.5	135	99.6	182	119.8
4pic (5.85)	124	96.2	170	112.5	121	94.5	140	101.7	181	119.9
mim (6.82)	-	-	174	117.2	-	-	173	116.3	175	117.4

Comparing the AN values (Figure 3), for systems with pyridine-based donors (py, 3pic, 4pic), the same pattern was observed, with acidity dependent both on the molar ratio of MCl₃, and on the metal (Al or Ga). In contrast, all ionic liquids based on 1-methylimidazole (the strongest base, Table 1) had the same acidity, AN = 174±1. Apparently, for the strongest donor, a 'naked' [BCl₂(mim)]⁺ cation is formed, as reflected in the constant, high, AN values. In contrast, borenium cations with weaker donors (py, 3pic, 4pic) interacted strongly with the anions resulting in anion-dependent AN values, with the least coordinating anion, [Ga₃Cl₁₀]⁻, affording the highest acidity. This distinction is unexpected, taking into consideration apparently full halide abstraction in all L-BCl₃-2MCl₃ systems, inferred from ¹¹B NMR spectra.

In conclusion, ionic liquids containing borenium cations, [BCl₂L]⁺, were demonstrated to be the strongest Lewis acids reported to date, with Acceptor Number values up to 182. Their Lewis acidity appears to be much higher than that from corresponding solution studies, e.g. AN = 80-85 found for [B(C₆F₅)₂]⁺ in CD₂Cl₂, or δ_{31P} = 106.9 ppm recorded for the [CatB]⁺ cation (cat = catecholato).^[22,31] offering the exciting prospect harnessing the full acidity of these 'naked' borenium cations in the ionic liquid state.

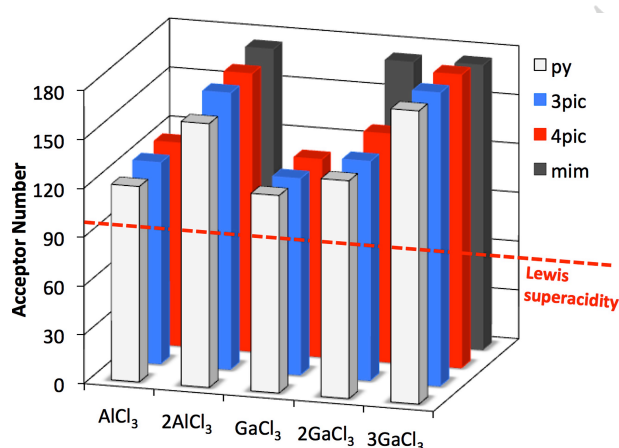


Figure 3. AN values for borenium cations, measured for L-BCl₃-nMCl₃ systems

Experimental Section

Triethylphosphine was provided by Cytec, all other reactants were purchased from Sigma-Aldrich. Solvents, and bases were dried over molecular sieves (3 Å) and stored under argon. Triethylphosphine oxide was dried (70 °C, 2 days, 10⁻² mbar) and stored in glovebox. Metal halides (anhydrous, in glass ampoules) and triethylphosphine were used as received. **Boron trichloride adducts** were prepared using an argon Schlenk line, by drop-wise addition of a base (0.9 mol eq.) to the vigorously stirred mixture of boron trichloride (1 M solution in heptane, 1.0 mol eq.) and DCM, at -78 °C. After reaction (-78 °C, 30 min, 600 rpm), excess reactants and solvents were removed under reduced pressure, and the adduct dried under high vacuum (60 °C, 10⁻² bar, overnight). Complexes of pyridine and picolines were recrystallised from a mixture of dry dichloromethane and hexane. **Borenium ionic liquids** were synthesized in a nitrogen-filled glovebox. Metal(III) chloride (1, 2 or 3 mol eq.) was added slowly to the boron trichloride adduct (1 mol eq.), and left to react until homogenous mixture was obtained, or no further change was observed (30-50 °C, 10 min - 24 h, 600 rpm). **NMR spectroscopy.** Boron trichloride adducts were measured as solutions in *d*-chloroform, the ionic liquids as neat liquids, with sealed capillaries of d₆-DMSO as an external lock. ¹¹B, ²⁷Al and ³¹P NMR spectra were recorded using a Bruker AvanceIII 400 MHz spectrometer. Background from the borosilicate tube was removed for ¹¹B NMR spectra using iNMR (Mestrelab Research). To determine **Acceptor Number**, three solutions of triethylphosphine oxide (tepo) in an ionic liquid were prepared, at concentrations of ca. 1, 2 and 3%. ³¹P NMR spectra were recorded neat, with d₆-DMSO as an external lock, and referenced to H₃PO₄, 85% ($\delta_{H_3PO_4}$ 85% = 0 ppm). The ³¹P NMR chemical shift at infinite dilution of tepo, δ_{inf} , was determined by extrapolation from ³¹P NMR chemical shifts at three different tepo concentrations and normalised to the chemical shift of tepo in hexane at infinite dilution ($\delta_{inf, hex}$ = 0 ppm). The AN values for all samples were calculated from: AN = 2.348 · δ_{inf} .

Acknowledgements

QUILL and its Industrial Advisory Board are acknowledged for financial support. MSK acknowledges QUB Research Fellowship scheme for funding. Cytec Industries Inc. are acknowledged for kindly providing phosphine ligands free of charge.

Keywords: Lewis superacids • borenium cations • ionic liquids • group 13 • acceptor number

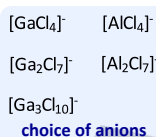
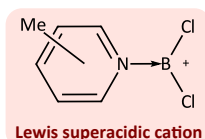
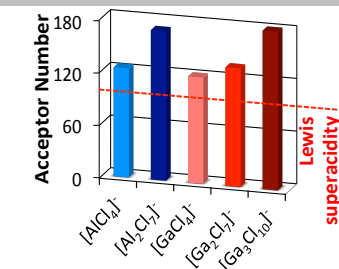
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Entry for the Table of Contents

COMMUNICATION

Borenium Lewis superacids:

Solventless synthesis of ionic liquids based on borenium cations and chlorometallate anions afforded a new class of liquid Lewis superacids, with acceptor numbers up to 182. The Lewis acidity was enhanced by the absence of a solvent, allowed by the ionic liquid environment.



Sesime Coffie, James M. Hogg, Lucie Cailler, Albert Ferrer-Ugalde, Richard W. Murphy, John D. Holbrey, Fergal Coleman,* and Małgorzata Swadźba-Kwaśny*

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